

## PATENT ABSTRACTS OF JAPAN

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### (54) COMPOSITION CURABLE BY ACTINIC RADIATION

#### (57)Abstract:

**PURPOSE:** To obtain the subject composition which is rapidly curable in a wide viscosity range to give a cured material having good adhesiveness and excellent hardness, tensile strength, extensibility, heat resistance and chemical resistance.

**CONSTITUTION:** This composition consists of a compound having at least two oxetane rings in the molecule, a compound having at least one oxirane ring in the molecule, and a compound that initiates cationic polymerization by irradiation with actinic radiation.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the activity energy-line hardening setup-of-tooling product which gives the hardened material which hardened promptly by the exposure of activity energy lines, such as ultraviolet rays or an electron beam, and was excellent in adhesion with a substrate.

[0002]

[Description of the Prior Art]In various industries, such as coating of the various characteristics, such as the quick cure rate, good workability by generally being a non-solvent, and a very low energy requirement, to wood, metal paint, and printing, activity energy-line hardening art is very important. In the early development in this field, research is concentrating on the activity energy-line start radical polymerization for polyfunctional acrylate, unsaturated polyester, etc., and such materials are still used in large quantities even today. Also in the present, although most of these researches are turned to the activity energy-line start radical polymerization, optical start being also ionic polymerization and being also quite promising in many applicable fields are fully admitted. Since especially optical start cationic polymerization is rich in various possibilities of chemical and realizing a physical characteristic, by the polymerization of various monomers, it is attractive. Since a polymerization is not checked by oxygen, it is not necessary to carry out optical start cationic polymerization under an inert atmosphere, and it has the advantage that a prompt and perfect polymerization can be performed in the air. Development of optical start cationic polymerization art was concentrated on two kinds of monomers called the epoxy resin and vinyl ether compound which have an oxirane ring which is 3 membered-ring cyclic ether till today. Especially a photoresist epoxy resin is excellent in an adhesive property, the hardening layer is excellent in hardness, tensile strength, and elongation, its heat resistance is high, and excelling in various physical properties, like chemical resistance is good

and there is known. However, the conventional photoresist epoxy resin has a defect in which photo-curing speed is comparatively slow, and, for this reason, prompt photo-curing was not able to use it for required paper or a use like coating of a plastic. Therefore, to raise a cure rate had been desired, employing the characteristic of an epoxy resin efficiently. Although these epoxy resins have many which have high viscosity and the method of reducing viscosity by blending a monofunctional epoxy resin etc. as reactive diluent for this reason is tried, If it is going to make viscosity into practical viscosity, i.e., 5000 cps, it has the problem that a cure rate will fall further. Polyfunctional epoxide to which the polyfunctional oxetane monomer which has two or more oxetane rings which are 4 membered-ring cyclic ether as a polymerization nature functional group in recent years is equivalent, and equivalent, or -- having a photoresist beyond it is reported (journal OBU macromolecular science .A -- 915 pages No. 10 29 volumes in 1992.) The photo-curing setup-of-tooling product which uses a polyfunctional oxetane monomer as the main ingredients is proposed as what has quick hardenability in said A30 volume, No. 2&3, 189 pages, and 1993 in said A30 volume, No. 2&3, 173 pages, and 1993 (Japanese Patent Application No. No. 49907 [ five to ]).

[0003]

[Problem(s) to be Solved by the Invention]However, although the cure rate at the time of using the above-mentioned polyfunctional oxetane monomer is quick as compared with an epoxy resin, it is still far slow in comparison with an acrylic activity energy-line radical polymerization. For this reason, although the photo-curing type resin which uses cyclic ether like an oxirane ring or an oxetane ring as a polymerization nature group had good heat resistance, an adhesive property, and chemical resistance, it was difficult for prompt photo-curing to apply to a required use. As for the purpose of this invention, the constituent, at i.e., the time of short, which solves the above-mentioned problem polymerizes by the optical exposure of a question, The hardened material which has and forms prompt hardenability in a wide range viscosity field is providing the activity energy-line hardening setup-of-tooling product which has a good adhesive property and is excellent in hardness, tensile strength, elongation, heat resistance, and chemical resistance.

[0004]

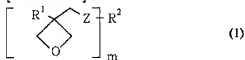
[Means for Solving the Problem]A compound which has two or more oxetane rings in a molecule as a result of this invention persons' inquiring wholeheartedly in view of such the actual condition, And an activity energy-line hardening setup-of-tooling product which consists of a compound which has one or more oxirane rings in a molecule maintains the good various characteristics of a hardened material, and also found out having quicker hardenability as compared with a compound which has the used oxetane ring, and completed this invention. That is, this invention relates to an activity energy-line hardening setup-of-tooling product which consists of a compound which makes cationic polymerization start by the exposure of a

compound which has two or more oxetane rings in a molecule, a compound which has one or more oxirane rings in a molecule, and an activity energy line. A constituent of this invention maintaining the characteristic which an activity energy-line hardening setup-of-tooling product which used the conventional epoxy resin had that heat resistance is high, excel in an adhesive property, and coating with good chemical resistance is obtained. Even if quick hardening has the high hardenability which can be equivalent also to a use demanded and is in hypoviscosity further, it makes to have fast curability into the feature. Although a constituent of this invention consists of a compound which has an oxirane ring, and a compound which more generally than this has an oxetane ring with a large cure rate, A cure rate as a constituent is possible for a thing equivalent to a cure rate of the compound itself which has the used oxetane ring which it is, and it carries out and is considered as an outstanding thing beyond it, and that of such a cure rate that stood high being brought about is very unexpected. This invention is explained in detail below.

[0005]O In compound this invention which has two or more oxetane rings in a molecule, as a compound (henceforth compound A) which has two or more oxetane rings in a molecule, various things can be used and a compound expressed with a following formula (1) can be mentioned as a desirable compound.

[0006]

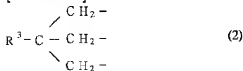
[Formula 1]



[0007]Here, in a formula (1), m is 2, 3, or 4 and Z is oxygen or sulfur. R<sup>1</sup> is the alkyl group of 1-6 carbon numbers, such as hydrogen, fluoride, a methyl group, an ethyl group, a propyl group, and a butyl group, a fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, or a furil group. R<sup>2</sup> is the linearity or the branching alkylene group, the linearity, or the branching poly (alkyleneoxy) group of the carbon numbers 1-12 shown, for example by a lower formula (2).

[0008]

[Formula 2]

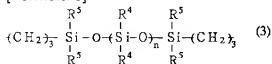


In the above-mentioned formula (2), R<sup>3</sup> are low-grade alkyl groups, such as a methyl group, an ethyl group, or a propyl group.

[0009]R<sup>2</sup> may also be a multivalent basis chosen from a group which consists of following (3), (4), and (5).

[0010]

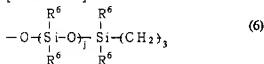
[Formula 3]



[0011]In a formula (3), n is an integer of 0-2000. R<sup>4</sup> is a basis chosen from the group which comprises the alkyl group of 1-10 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or a butyl group, and following (6).

[0012]

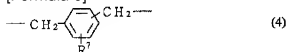
[Formula 4]



[0013]In a formula (6), j is an integer of 0, or 1-100, and R<sup>6</sup> is alkyl which has 1-10 carbon atoms. R<sup>5</sup> is an alkyl group of the carbon numbers 1-10, such as a methyl group, an ethyl group, a propyl group, or a butyl group.

[0014]

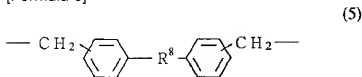
[Formula 5]



[0015]In a formula (4), R<sup>7</sup> is the alkyl group of 1-10 carbon numbers, such as hydrogen, a methyl group, an ethyl group, a propyl group, or a butyl group, the alkoxy group of 1-10 carbon numbers, a halogen atom, a nitro group, a cyano group, a sulfhydryl group, a low-grade alkyl carboxylate group, or a carboxyl group.

[0016]

[Formula 6]

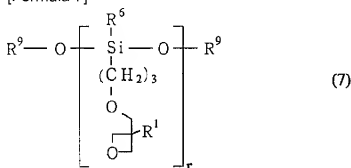


[0017]In a formula (5), R<sup>8</sup> is oxygen, sulfur, NH, SO, SO<sub>2</sub>, CH<sub>2</sub>, C(CH<sub>3</sub>)<sub>2</sub>, or C(CF<sub>3</sub>)<sub>2</sub>. The

thing of a low-grade alkyl group has preferred  $R^1$ , and the thing of an ethyl group is [ in / at this invention / the above-mentioned formula (1) ] more preferred. As  $R^2$ , the thing of an ethyl group has preferred  $R^3$  in the basis, hexamethylene group, and formula (2) whose  $R^7$  is a hydrogen atom in a formula (4).  $R^5$  and  $R^6$  are methyl preferably. Z is oxygen preferably. As other desirable examples of compound A, the compound of a formula (7) and a formula (8) can be mentioned.

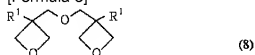
[0018]

[Formula 7]



[0019]

[Formula 8]



[0020] In a formula (7), r is an integer of 25-200 and  $R^9$  is the alkyl group or trialkylsilyl group of the carbon numbers 1-4.

[0021] In this invention, two or more kinds of the above-mentioned compounds A can be used together.

[0022] O The oxirane ring in which the compound (henceforth the compound B) which has one or more oxirane rings in the molecule used into a molecule by compound this invention which has one or more oxirane rings is shown by one or more lower formulas in a molecule [0023]

[Formula 9]



[0024] It is a compound which \*\*\*\*, and if used as an epoxy resin, it is usually usable in either a monomer oligomer or polymer. As an example of the compound B, publicly known aromatic epoxy resin, an alicycle fellows epoxy resin, and an aliphatic series epoxy resin are mentioned conventionally. An epoxy resin means a monomer, oligomer, or polymer below. A thing desirable as aromatic epoxy resin is JI or poly glycidyl ether manufactured by the reaction of

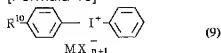
polyhydric phenol which has at least one aromatic core, or its alkylene oxide adduct and epichlorohydrin, For example, JI of JI of bisphenol A or its alkylene oxide adduct or poly glycidyl ether, hydrogenation bisphenol A, or its alkylene oxide adduct or poly glycidyl ether, novolak type epoxy resin, etc. are mentioned. Ethyleneoxide or propylene oxide is mentioned as alkylene oxide here. As an alicycle follows epoxy resin, a compound which has cycloalkane rings, such as KISEN or a cyclopentene ring, to at least one cyclo, Cyclohexene oxide or a cyclopentene oxide content compound obtained by epoxidating with suitable oxidizers, such as hydrogen peroxide and a peroxy acid, has it, and as an example, [ preferred ] 3, the 4-epoxycyclohexylmethyl 3, 4-epoxycyclohexylcarboxylate, etc. are mentioned. As a desirable thing of an aliphatic series epoxy resin, There is JI or poly glycidyl ether of aliphatic polyhydric alcohol or its alkylene oxide adduct, etc., and as the example of representation, Diglycidyl ether of ethylene glycol, diglycidyl ether of propylene glycol, or diglycidyl ether of alkylene glycol, such as diglycidyl ether of 1,6-hexanediol, Poly glycidyl ether of polyhydric alcohol, such as JI of glycerin or its alkylene oxide adduct, or triglycidyl ether, Diglycidyl ether of polyalkylene glycols, such as a polyethylene glycol or diglycidyl ether of the alkylene oxide adduct, a polypropylene glycol, or diglycidyl ether of the alkylene oxide adduct, etc. are mentioned. Ethyleneoxide or propylene oxide is mentioned as alkylene oxide here. Monoglycidyl ether of aliphatic higher alcohol which is a monomer which has one oxirane ring, phenol, cresol or monoglycidyl ether of such alkylene oxide adducts, etc. can be used for intramolecular other than these compounds.

[0025] In this invention, two or more kinds of the above-mentioned compounds B can be used together.

[0026] Various \*\*\*\* for cationic photopolymerization initiators conventionally publicly known as a compound (henceforth the compound C) which makes cationic polymerization start by the exposure of a compound activity energy line which makes cationic polymerization start by the exposure of an activity energy line -- things are made. As a desirable thing, diaryliodonium salt and a triarylsulfonium salt are mentioned among these initiators. A typical photopolymerization initiator is shown below.

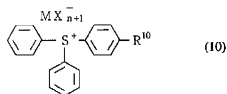
[0027]

[Formula 10]



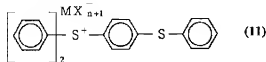
[0028]

[Formula 11]



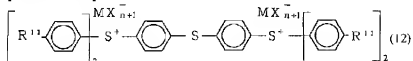
[0029]

[Formula 12]



[0030]

[Formula 13]



[0031]  $\text{R}^{10}$  is hydrogen, an alkyl group of various length of the carbon numbers 1-18, or an alkoxy group of the carbon numbers 1-18 among a formula -- M -- metal -- it is antimony preferably -- X -- halogen -- it is fluoride preferably, and n is a metaled valence, for example, in the case of antimony, it is 5.  $\text{R}^{11}$  are hydrogen, a hydroxyalkyl group, and a hydroxyalkoxy group, and are a hydroxyethoxy basis preferably.

[0032] O Inerts like an inorganic bulking agent, a color, paints, a viscosity modifier and a processing agent, and an ultraviolet-rays interception agent besides the above-mentioned essential ingredient can be blended with the constituent of other ingredient this inventions.

[0033] When stiffening a constituent of this invention by visible light, or when making it harden by ultraviolet rays, in addition to the compound C, a photosensitizer can also be blended in order to improve hardenability further. As for a typical sensitizer which can be used in this invention, Crivello is ADOBANSUDO. Yne Polymer science It is possible to use a compound currently indicated by Adv. in Plymer Sci., and [62, 1] (1984). As an example, there are pyrene, perylene, an acridine orange, a thioxan ton, 2-chloro thioxan ton, and a PENZO flavin.

[0034] O What is necessary is just to mix the above-mentioned compound A, and B and C in accordance with a conventional method as a manufacturing method of an activity energy-line hardening setup-of-tooling product of manufacturing method this invention. Here, as for compound A, it is preferred to carry out 5-80 weight-section combination to total quantity 100 weight section of compound A in a constituent and the compound B. Hardenability becomes less enough, when hypoviscosity-izing of a constituent becomes insufficient when loadings of



compound A are less than five weight sections and it exceeds another side 80 weight section. As for the compound C, it is preferred to carry out 0.01-20 weight-section combination to total quantity 100 weight section of compound A and the compound B, and it is 0.1 to 10 weight section more preferably. In fully being unable to stiffen a constituent when loadings are less than 0.01 weight sections, and exceeding 20 weight sections, there is a case where a light transmittance state becomes poor and uniform hardening becomes impossible. What is necessary is just to determine each concrete compounding ratio of compound A and the compound B in consideration of various physical properties, such as viscosity of a constituent demanded in a mentioned range, and hardness of a hardened material.

[0035]O Harden easily a constituent in which the quick hardenability of directions-for-use this invention is shown by irradiating with activity energy lines, such as ultraviolet rays, X-rays, or an electron beam. When irradiating with ultraviolet rays, various light sources can be used, for example, it can be made to harden by mercury arc lamp, xenon arc lamp, fluorescent lamp, carbon arc lamp, a tungsten halogen copy lamp, and irradiation light from the surrounding daylight. Irradiation intensity of ultraviolet rays is a 0.01 W square centimeter at least. When hardening continuously with paper or a metallic coating line, it is preferred to set up exposure speed so that a constituent can be hardened within 1 to 20 seconds. When making it harden with an electron beam, it is made to usually harden with an electron beam of the following 300-eV energies, but it is possible to also make it harden in an instant with a dose of 1Mrad - 5Mrad.

[0036]A constituent of this invention is applicable to substrates, such as metal, rubber, a plastic, forming parts, a film, paper, a tree, a woven glass fabric, concrete, and ceramics.

[0037]As a use of a constituent of this invention, protection, an ornament and coating for an insulation, encapsulant, printer's ink, sealant, adhesives, photoresist, a wire insulating material, textile coating, a lamination, an impregnated tape, a printing plate, etc. are mentioned, for example.

[0038]

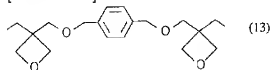
[Example]An example and a comparative example are given to below, and this invention is more concretely explained to it. Compounds A other than the compound shown with the following formula (13) and (14), for example, -- in a formula (1), m is 3 and Z is an oxygen atom --  $R^1$  -- low-grade alkyl -- it being an ethyl group preferably and, it is a polyfunctional basis  $R^2$  is indicated to be by a formula (2) -- and  $R^3$  -- low-grade alkyl -- in the compound which is an ethyl group preferably, or a formula (8) --  $R^1$  -- low-grade alkyl -- the constituent which blended the compound which is an ethyl group preferably is also useful.

[0039]as example 1 compound A -- the compound (13) of a following formula -- 75 copies (a weight section.) Below, to the same constituent that mixed 25 copies of bisphenol A diglycidyl

ether as the compound B, 2,5-copy addition mixing of the diphenyl-4-thio phenoxyphenyl sulfoniumhexafluoroantimonate was carried out as the compound C, and the activity energy-line hardening setup-of-tooling product was prepared.

[0040]

[Formula 14]

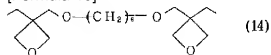


[0041]The viscosity of the obtained constituent was measured at 25 °C using the Brookfield viscometer. A black light of the conveyor type which installed the condensed type high-pressure mercury-vapor lamp of 80 w/cm after applying this constituent so that it may become about 20 microns to a steel plate (lump height = 10 cm) Irradiation intensity: Using 310-mW/cm<sup>2</sup> and 76 mJ/cm<sup>2</sup>, conveyor speed was changed, the greatest speed those of stickiness lost from the surface was measured, and this was made into hardenability. About the obtained hardened material, crosscut back tape exfoliation was carried out, and adhesion was evaluated, and pencil hardness was measured according to JIS K5400. The upper PET film was put on the glass plate, and the rubber sheet with a thickness of 1 mm was further carried for the hole of the bumb bell shape on this. After slushing a constituent into the hole of a bumb bell shape, a PET film and glass were carried on this. UV irradiation was carried out to this for 3 minutes at a time at the surface and the rear face using the scattered-light type black light (lump height = 25 cm) of 60 w/cm. The glass plate and the PET film were removed after this, and the surface and the rear face of the hardened material of the bumb bell shape were irradiated with ultraviolet rays for 3 minutes at a time. About the obtained hardened material, tensile strength and elongation were measured according to JIS K6301.

[0042]Said compound (13) or the compound (14) of the following formula was used as the compound B as Example 2 - 6 compounds A by the composition ratio which showed bisphenol A diglycidyl ether in Table 1, respectively, and the constituent was prepared like Example 1. It evaluated like [ constituent / which was obtained ] Example 1. The result is shown in Table 1 and 2.

[0043]

[Formula 15]



[0044]

[Table 1]

実施例	化合物A〔部〕	化合物B〔部〕	粘度(cps/25℃)
1	化合物(13) 〔75〕	ビスフェノールA〔25〕 ジグリシジルエーテル	148
2	同上〔50〕	同上〔50〕	538
3	同上〔25〕	同上〔75〕	2360
4	化合物(14) 〔75〕	同上〔25〕	32
5	同上〔50〕	同上〔50〕	122
6	同上〔25〕	同上〔75〕	768
7	同上〔10〕	同上〔90〕	4300

[0045]

[Table 2]

実施例	硬化性 (m/min)	密着性	鉛筆硬度	引張強度 (kg/cm <sup>2</sup> )	伸び (%)
1	20	○	H	430	5以下
2	40以上	○	2H	576	5以下
3	40以上	○	H	454	5以下
4	6	○	2B	263	5以下
5	8	○	B	287	5以下
6	10	○	H	525	5以下
7	20	○	H	711	5以下

[0046]As shown in the comparative example 1 and the two tables 3, it was used with a said compound (13) independent, and the constituent was prepared like Example 1. It evaluated like [ constituent / which was obtained ] Example 1. The result is shown in Table 3 and 4.

[0047]

[Table 3]

比較例	化合物A〔部〕	化合物B〔部〕	粘度(cps/25℃)
1	化合物(13) 〔100〕	0	65

[0048]

[Table 4]

比較例	硬化性 (m/min)	密着性	鉛筆硬度	引張強度 (kg/cm <sup>2</sup> )	伸び (%)
1	4以下	測定不能	測定不能	232	5以下

[0049]As shown in the two to comparative example 5 table 5, a compound B independent or a compound B mixture was used, and the constituent was prepared like Example 1. It evaluated like [ constituent / which was obtained ] Example 1. The result is shown in Table 5 and 6.

[0050]

[Table 5]

比較例	化合物B〔部〕		粘度(cps/25℃)
2	ビスフェノールA〔100〕 ジカリスリルエーテル	0	14000
3	同上〔75〕	ヘキシルシクアリ ジシスエーテル〔25〕	653
4	同上〔50〕	同上〔50〕	134
5	同上〔25〕	同上〔75〕	28

[0051]

[Table 6]

比較例	硬化性 (m/min)	密着性	鉛筆硬度	引張強度 (kg/cm <sup>2</sup> )	伸び (%)
2	8	○	H	7 7 0	5以下
3	4以下	測定不能	測定不能	5 2 1	5以下
4	4以下	測定不能	測定不能	3 9 4	5以下
5	4以下	測定不能	測定不能	2 4 3	5以下

[0052]

[Effect of the Invention]Cure fast the activity energy-line hardening setup-of-tooling product of this invention by the activity energy-line exposure of ultraviolet rays or an electron beam, and excel in adhesion with a substrate, and Since the hardened material has still better various physical properties, The influence which can be used for various uses, such as protection, an ornament and coating for an insulation, a \*\*\*\* compound, printer's ink, sealant, adhesives, photoresist, a wire insulating material, textile coating, a lamination, an impregnated tape, and a printing plate, and it has on the industrial world is size.

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[Translation done.]